Acid-Catalyzed Rearrangement of [*m*.3.2]Propellanols†

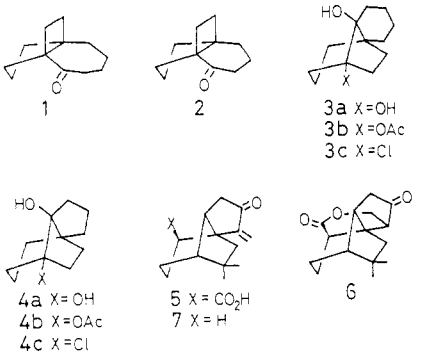
Kiyomi Kakiuchi,* Toshinori Tsugaru, Mitsunori Takeda, Itsuyo Wakaki, Yoshito Tobe, and Yoshinobu Odaira

Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received June 18, 1984

The acid-catalyzed rearrangement of *exo*-[5.3.2]propellanol (**8x**) gave (1*S**,6*R**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecane derivatives **22** and **23**, while endo alcohol **8n** gave (1*S**,6*S**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecane derivatives **24** and **25**, both by 1,2-alkyl shifts of the central propellane bonds. Similarly, *exo*-[4.3.2]propellanol (**9x**) rearranged in acid to (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecane derivatives **32** and **33** via 1,2-alkyl shift of the central propellane bond. On the other hand, endo alcohol **9n** yielded (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecan-5-ol (**38**) as the initial reaction product via 1,2-alkyl shift of the external cyclobutane bond. However, **38** underwent a second alkyl shift to give as major products the *cis*,*cis*-tricyclo[6.3.0.0^{1,5}]undecane derivatives **39** and **40**. The structures of these products were established by chemical transformations.

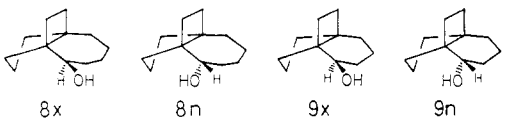
We recently reported the acid-catalyzed rearrangement of [5.3.2]- and [4.3.2]propellanones (**1** and **2**) to tricyclo[5.3.2.0^{1,6}]dodecane derivatives **3a,b** and tricyclo[4.3.2.0^{1,5}]undecane derivatives **4a,b**, respectively, through 1,2-alkyl shift of the central propellane bond.[1] This rearrangement provides a one-step construction of the carbocyclic skeleton of terrecyclic acid (**5**)[2] and quadrone (**6**),[3]



which are of interest because of their unusual structures and biological activities. We have also synthesized descarboxyquadrone (**7**),[4] from a [4.3.2]propellanone derivative by this acid-catalyzed rearrangement.[5]

Two ways in which the central bond of [*m*.3.2]propellanones can migrate are shown in Scheme I. Path a proceeds through cation **10**, with an endo hydroxyl group, to give the tricyclic alcohol **12**. Path b affords the tricyclic alcohol **13**, which has an exo hydroxyl group. It was found in previous work[1b] that the acid-catalyzed rearrangement of [*m*.3.2]propellanones **1** and **2** in nucleophilic media proceeds through path a to give **3a**, **3b**, **4a**, and **4b**.

We describe here the acid-catalyzed rearrangement of *exo*- and *endo*-[5.3.2]propellanols (**8x** and **8n**) and *exo*- and

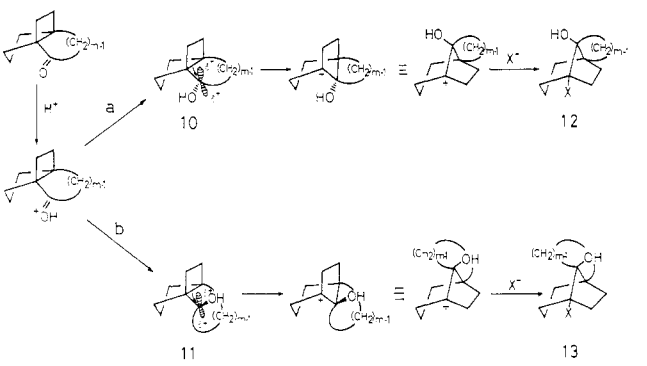


endo-[4.3.2]propellanols (**9x** and **9n**) in order to investigate this rearrangement in further detail.[6] The cations formed from these compounds in the presence of acid should be similar to cations **10** and **11** and should form analogues of **12** and **13**.

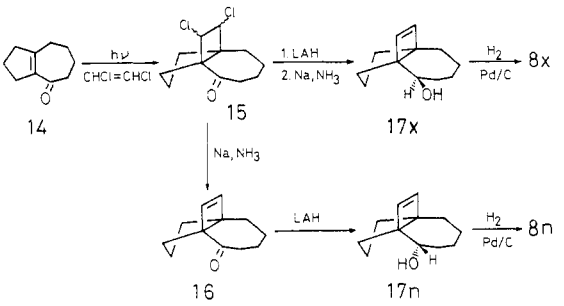
Results and Discussion

Synthesis of *exo*- and *endo*-Propellanols 8x, 8n, 9x, and 9n. The reduction of [5.3.2]propellanone (**1**) with

Scheme I



Scheme II



various hydride reagents gave both exo and endo alcohols **8x** and **8n**.[7] However, since they could not be separated

† Presented at 47th Annual Meeting of the Chemical Society of Japan, Kyoto, April 1983 (Abstracts, Vol 2, p 882), and 16th Symposium on Structural Organic Chemistry, Saitama, Sept 1983 (Abstracts, p 269).

(1) (a) Kakiuchi, K.; Hato, Y.; Tobe, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 6. (b) Kakiuchi, K.; Itoga, K.; Tsugaru, T.; Hato, Y.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1984**, *49*, 659.

(2) Isolation; Nakagawa, M.; Hirota, A.; Sakai, H. *J. Antibiot.* **1982**, *35*, 778. Synthesis; Kon, K.; Ito, K.; Isoe, S. *Tetrahedron Lett.* **1984**, *25*, 3739.

(3) Isolation: (a) Ranieri, R. L.; Calton, G. J. *Tetrahedron Lett.* **1978**, 499. (b) Calton, G. J.; Ranieri, R. L.; Espenshade, M. A. *J. Antibiot.* **1978**, *31*, 38. Synthesis: (c) Danishefsky, S.; Vaughan, K.; Gadwood, R. C.; Tsuzuki, K. *J. Am. Chem. Soc.* **1981**, *103*, 4136. (d) Bornack, W. K.; Bhagwat, S. S.; Ponton, J.; Helquist, P. *Ibid.* **1981**, *103*, 4647. (e) Burke, S. D.; Murtiashaw, C. W.; Sanders, J. O.; Dike, M. S. *Ibid.* **1982**, *104*, 872. (f) Kende, A. S.; Roth, B.; Sanfilippo, P. J.; Blacklock, T. J. *Ibid.* **1982**, *104*, 5808. (g) Takeda, K.; Shimono, Y.; Yoshii, E. *Ibid.* **1983**, *105*, 563. (h) Schlessinger, R. H.; Wood, J. L.; Poss, A. J.; Nugent, R. A.; Parsons, W. H. *J. Org. Chem.* **1983**, *48*, 1146. (i) Burke, S. D.; Murtiashaw, C. W.; Oplinger, J. A. *Tetrahedron Lett.* **1983**, *24*, 2949. (j) Dewanckele, J. M.; Zutterman, F.; Vandewalle, M. *Tetrahedron* **1983**, *39*, 3235. Skeleton synthesis: (k) Monti, S. A.; Dean, T. R. *J. Org. Chem.* **1982**, *47*, 2679. (l) Paquette, L. A.; Annis, G. D.; Schostarez, H. *J. Am. Chem. Soc.* **1982**, *104*, 6646.

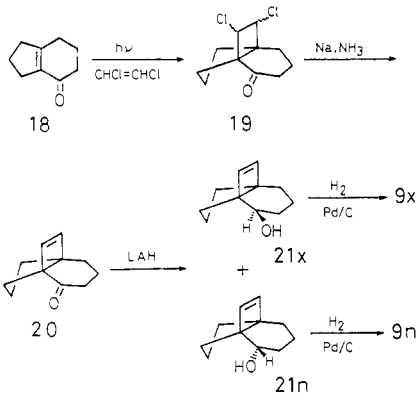
(4) Smith, A. B., III; Wexler, B. A.; Slade, J. *Tetrahedron Lett.* **1982**, *23*, 1631.

(5) Kakiuchi, K.; Nakao, T.; Takeda, M.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1984**, *25*, 557.

(6) When this article was going to be submitted, the acid-catalyzed rearrangement of **9x** and **9n** was just reported by Smith et al.: Smith, A. B., III; Wexler, B. A. *Tetrahedron Lett.* **1984**, *25*, 2317.

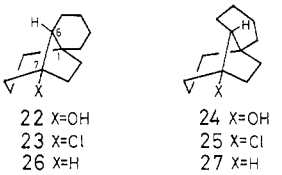
0022-3263/85/1950-0488$01.50/0

Scheme III



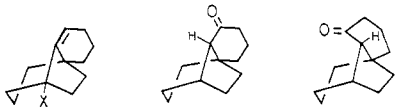
by GLC or column chromatography on silica gel, we explored an alternative route to obtain them stereoselectively. Photoreaction of bicyclo[5.3.0]dec-1(7)-en-2-one (**14**) with 1,2-dichloroethylene (trans and cis mixture) at room temperature gave cycloadducts **15**[8] (1:1 ratio) in 41% yield. Reduction of **15** with $LiAlH_4$ and subsequent reduction with Na–NH_3 afforded *exo*-[5.3.2]propellenol (**17x**) in 84% yield as the sole product. Reversing the sequence of the two reductions gave only *endo*-[5.3.2]propellenol (**17n**) in 30% yield. The configuration of the hydroxyl groups in **17x** and **17n** was established by ^1H NMR spectra using the shift reagent $Eu(dpm)_3$. The *S* values[9] for the vinyl protons of **17x** were 10.8 and 4.7 while those of **17n** were 6.9 and 3.6. The difference in the direction of hydride access is attributed to steric hindrance at the exo side of **15** due to the chlorine atoms[8] and to steric accessibility at the same side of **16** due to the vinyl group. Finally, hydrogenation of **17x** or **17n** with palladium on charcoal gave **8x** or **8n** in 85–88% yields (Scheme II). *exo*- and *endo*-[4.3.2]propellanols (**9x** and **9n**)[10] were prepared in a similar way. Photocycloaddition of dichloroethylene to bicyclo[4.3.0]non-1(6)-en-2-one (**18**) gave cycloadducts **19** (2:93:5 ratio) in 94% yield. Reduction of **19** with Na–NH_3 afforded [4.3.2]propellenone (**20**) in 53% yield and subsequent $LiAlH_4$ reduction gave a mixture of *exo*- and *endo*-[4.3.2]propellenols (**21x** and **21n**) (3:1) in 86% yield, which were separated by column chromatography on silica gel.[11] The stereochemistry of the hydroxyl groups of **21x** and **21n** was also determined by LIS ^1H NMR; the *S* values[9] for the vinyl protons of **21x** were 11.9 and 5.2, while those of **21n** were 5.4 and 3.5. Hydrogenation of **21x** and **21n** gave **9x** and **9n**, respectively (Scheme III).

Acid-Catalyzed Rearrangement of *exo*- and *endo*-[5.3.2]Propellanols (8x and 8n). Treatment of exo alcohol **8x** with H_2SO_4 in aqueous THF at room temperature for 24 h gave (1*S**,6*R**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecan-7-ol (**22**) in 87% yield. Also, reaction of **8x** with concentrated HCl in ether at room temperature for 24 h afforded **22** (79%) together with the corresponding chloride **23** (12%). On the other hand, treatment of endo alcohol **8n** with H_2SO_4 at 55 °C for 48 h gave (1*S**,6*S**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecan-7-ol (**24**) in 77% yield, and reaction with concentrated HCl (reflux, 24 h) furnished **24** and the



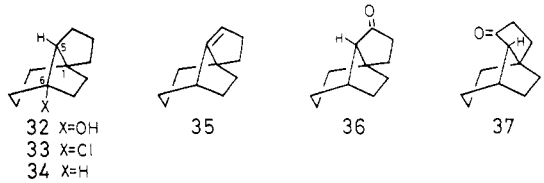
chloride **25** in 78% and 10% yields, respectively. Thus, the stereochemistry at C-6 of the tricyclododecanes **22** and **23** derived from **8x** was different from that of **24** and **25** derived from **8n**. The rearrangement of **8n** required higher reaction temperatures than **8x**.

The structures of **22–25** were elucidated by spectroscopic data and chemical transformations. Chlorination of **22** and **24** with thionyl chloride gave chlorides **23** and **25** in 82–90% yields, showing that both had the same carbon skeleton. Reduction of **23** and **25** with tri-*n*-butyltin hydride afforded the corresponding hydrocarbons **26** and **27**. That **26** and **27** were tricyclo[5.3.2.0^{1,6}]dodecane isomers was established by identity with authentic samples. The acid-catalyzed rearrangement of [5.3.2]propellanone (**1**) with concentrated HCl and subsequent dehydration of the alcohol **3c** gave the chloride **28**. Reduction of the chlorine atom of **28** followed by catalytic hydrogenation of the olefin **29** afforded a mixture of **26** and **27** (1:1). Moreover, hydroboration–oxidation of **29** followed by Collins oxidation gave (1*S**,6*R**,7*S**)-tricyclo[5.3.2.0^{1,6}]dodecan-5-one (**30**) and the 1*S**,6*S**,7*S** isomer **31** in a 1:4 ratio. Chromatography of this mixture on activated alumina converted **31** into **30**. Thus **30** is the thermodynamically more stable



ketone and is assigned 1*S**,6*R**,7*S** stereochemistry at C-6 because hydrocarbon **26** is estimated to be more stable by about 2 kcal/mol than **27**, based on the sum of the calculated strain energies[12] of *cis*-bicyclo[4.3.0]nonane and *trans*-bicyclo[4.4.0]decane and that of the corresponding trans and cis isomers. Since **30** was converted into **26** by thioketal reduction, **22**, **23**, and **26** should have 1*S**,6*R**,7*S** configuration at C-6, and therefore **24**, **25**, and **27** should be 1*S**,6*S**,7*S** isomers.

Acid-Catalyzed Rearrangement of *exo*- and *endo*-[4.3.2]Propellanols (9x and 9n). The H_2SO_4-catalyzed rearrangement of **9x** to (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecan-6-ol (**32**) has been reported.[6] Reaction of **9x** with concentrated HCl at reflux for 24 h afforded **32** and chloride **33** in 64% and 19% yields, respectively. The structures of **32** and **33** were established by the same



sequence of transformations used for **22–25**. Thus **32** was converted into **33** with thionyl chloride and **33** into **34** with tri-*n*-butyltin hydride. In addition, **35**, obtained from **2**,[5] was converted into a mixture of **36** and **37** and **37** rearranged to **36** during chromatography. Since Wolff–Kishner

(7) Reduction of **1** with $LiAlH_4$, $NaBH_4$, $LiBEt_3H$, and Dibal gave the corresponding alcohols **8x** and **8n** in almost quantitative yields (**8x**/**8n** = 0.6–2.2, determined by ^1H NMR spectra).

(8) The stereochemistry of **15** may be assumed to be cis–syn–trans and cis–anti–trans: Tobe, Y.; Hoshino, T.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1978**, *43*, 4334.

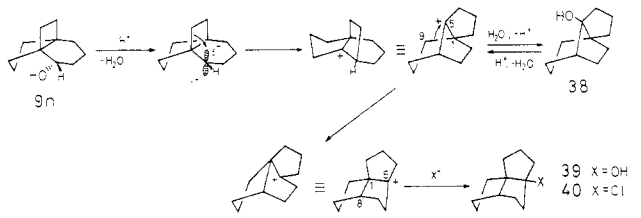
(9) Cockerill, A. F.; Rackham, D. M. *Tetrahedron Lett.* **1970**, 5149.

(10) Reduction of **2** with $LiAlH_4$ gave **9x** and **9n** (95% yield) in an about 4:1 ratio.

(11) Also, reduction of **20** with Dibal gave a mixture of **21x** and **21n** (81% yield) in an about 1.8:1 ratio.

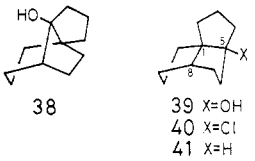
(12) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, S. M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.

Scheme IV



reduction of **36** gave hydrocarbon **34**, the stereochemistry of **34** at C-5 should be 1*S**,5*R**,6*S**.[13]

The rearrangement of **9n** with H_2SO_4 in aqueous THF has been reported to give (1*S**,5*R**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecan-5-ol (**38**) and *cis,cis*-tricyclo[6.3.0.0^{1,5}]undecan-5-ol (**39**).[6] Treatment of **9n** with concentrated HCl in ether at reflux for 24 h afforded a mixture of *cis,cis*-5-chlorotricyclo[6.3.0.0^{1,5}]undecane (**40**) (41%), (**38**

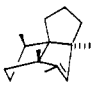


(23%), and **39** (8%). Chlorination of **39** with thionyl chloride afforded **40** (83%), showing that they have the same skeleton. Since **40** was reduced with tri-*n*-butyltin hydride to *cis,cis*-tricyclo[6.3.0.0^{1,5}]undecane (**41**) (92%) whose ^{13}C NMR spectrum was identical with that reported in the literature,[15] **39** and **40** should be *cis,cis*-tricyclo[6.3.0.0^{1,5}]undecan-5-yl derivatives. Moreover, reduction of (1*S**,5*R**,6*S**)-6-chlorotricyclo[4.3.2.0^{1,5}]undecan-5-ol (**4c**)[5] with tri-*n*-butyltin hydride gave **38** in quantitative yield, indicating that **38** has the same tricyclic skeleton as that of **32** derived from **9x**, but with the hydroxyl group attached at C-5.

From these results, it is deduced that the formation of **38** involves a 1,2-alkyl shift of the external bond of the cyclobutane ring followed by attack of the necleophile at C-5 from the backside of the developing p orbital as shown in Scheme IV.[16] The angular triquinanes **39** and **40** are derived from **38** by further rearrangement because the ratio of **39** increased at the expense of **38** with increasing reaction time, and treatment of **38** with H_2SO_4 in aqueous THF gave **39** in quantitative yield. We therefore infer that the formation of **39** and **40** involves the migration of C-9 to the cation center at C-5 followed by attack of a nucleophile (Scheme IV), in view of the mechanisms of tricycloundecane carbonium ion rearrangements based on molecular mechanics calculations.[14]

Although the exo alcohols **8x** and **9x** both rearrange by 1,2-akly shift of the central bond (path a), endo alcohols **8n** and **9n** rearrange in different ways. While **8n** rearranges by way of a 1,2-alkyl shift of the central bond (path b), **9n** rearranges by a 1,2-alkyl shift of the external bond. This difference is attributed to the difference in flexibility of the cycloalkanol rings. Since the seven-membered ring in **8n** is more flexible than the six-membered ring in **9n**, the developing p orbital of **8n** is capable of overlapping with the central propellane bond while that of **9n** is not. In other words, the transition state leading to the (1*S**,5*S**,6*S**)-tricyclo[4.3.2.0^{1,5}]undecan-6-yl cation seems to be highly strained.[14]

The rearrangement of **9n** provides an efficient route to tricyclo[6.3.0.0^{1,5}]undecane derivatives **39** and **40**, which have the basic skeleton of angular triquinane sesquiterpenes such as isocomene (**42**).[17] We are continuing to investigate this rearrangement.



42

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer as liquid films unless otherwise stated. Mass spectra were measured with a Hitachi RMU-6E spectrometer. ^{1}H NMR spectra were obtained on a JEOL JNM-PS-100 spectrometer in CCl_4, and ^{13}C NMR spectra were taken on a JEOL JNM-FX-60S spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC was conducted on a Varian Aerograph 920 gas chromatograph with a 10% FFAP column or 30% SE-30 column. Column chromatography was carried out on silica gel from Wako Pure Chemical Industries (Wakogel C-200, 100–200 mesh) unless otherwise stated.

Materials. [5.3.2]Propellanone (**1**), bicyclo[5.3.0]dec-1(7)-en-2-one (**14**), and bicyclo[4.3.0]non-1(6)-en-2-one (**18**) were prepared as described previously.[1b] Tricyclo[4.3.2.0^{1,5}]undec-4-ene (**35**) and (1*S**,5*R**,6*S**)-6-chlorotricyclo[4.3.2.0^{1,5}]undecan-5-ol (**4c**) were synthesized from [4.3.2]propellanone (**2**) in the previous work.[5]

***exo*-Tricyclo[5.3.2.0^{1,7}]dodec-11-en-2-ol (17x).** A solution of 13.4 g (89.3 mmol) of the enone **14** in 250 mL of 1,2-dichloroethylene (trans and cis mixture) was irradiated through a Pyrex filter at room temperature for 40 h. Disappearance of the enone was monitored by GLC. The excess dichloroethylene was removed in vacuo and the residue was distilled under reduced pressure to give the cycloadducts **15** (1:1 ratio): 8.70 g (41%); bp 135–160 °C (5 mm); IR 1680 cm^{-1}.

To a stirred suspension of 0.18 g (4.65 mmol) of lithium aluminum hydride in 60 mL of dry ether was added dropwise a solution of 2.30 g (9.30 mmol) of **15** in 25 mL of dry ether, and the mixture was stirred at room temperature for 1 h. Water was added carefully, and 10% HCl was subsequently added to dissolve the white precipitate. The organic layer was separated, and the aqueous solution was extracted with ether. The combined extracts were washed with saturated $NaHCO_3$ solution, brine, and dried ($MgSO_4$). The solvent was removed in vacuo to give the crude alcohols: IR 3350, 3420 cm^{-1}.

To a solution of the above alcohols in 20 mL of dry ether was introduced 340 mL of freshly distilled, anhydrous ammonia at −78 °C under nitrogen. Small pieces of sodium metal were added to the stirred solution until it remained dark blue. After the blue solution was stirred for an additional 1 h, ammonium chloride was added to destroy sodium, and the ammonia was allowed to evaporate at room temperature. Water was added to the residue, and the mixture was extracted with ether. The organic layer was dried ($MgSO_4$) and concentrated in vacuo followed by column chromatography to give the exo alcohol **17x**: 1.40 g (84% from **15**); mp 49–51 °C; IR (KBr) 3250, 3030, 3010, 1005, 750 cm^{-1}; MS, *m/e* (relative intensity) 178 (M$^+$, 34), 149 (100); ^{1}H NMR δ 0.90–2.12 (m, 15 H), 3.53 (dd, *J* = 3, 10 Hz, 1 H), 5.91 (AB q, *J*

(13) (1*S**,5*R**,6*S**)-Tricyclo[4.3.2.0^{1,5}]undecane (**34**) is estimated to have greater thermodynamic stability (5–6 kcal/mol) than the 1*S**,5*S**,6*S** isomer.[14]

(14) Osawa, E.; Aigami, K.; Takaishi, N.; Inamoto, Y.; Fujikura, Y.; Majerski, Z.; Schleyer, P. v. R.; Engeler, E. M.; Farcasiu, M. *J. Am. Chem. Soc.* **1977**, *99*, 5361.

(15) Takaishi, N.; Inamoto, Y.; Tsuchihashi, K.; Yashima, K.; Aigami, K. *J. Org. Chem.* **1975**, *40*, 2929.

(16) There are several precedents of this mode of migration involving ours:[1b] (a) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106. (b) Cargill, R. L.; Bryson, T. A.; Krueger, L. M.; Kempf, J. V.; McKenzie, T. C.; Bordner, J. *J. Org. Chem.* **1976**, *41*, 409. (c) Cargill, R. L.; Bushey, D. F.; Dalton, J. R.; Prasad, R. S.; Dyer, R. D.; Bordner, J. *Ibid.* **1981**, *46*, 3389. (d) Smith, A. B., III; Jerris, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 194. (e) Tobe, Y.; Hayauchi, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 5219.

(17) See recent reviews: (a) Yoshii, E.; Takeda, K. *J. Synth. Org. Chem. Jpn.* **1983**, *41*, 348. (b) Paquette, L. A. *Top. Curr. Chem.* **1979**, *79*, 41; **1984**, *119*, 1.

= 3, 2 H); ^{13}C NMR δ 141.03 (d), 136.40 (d), 77.84 (d), 65.14 (s), 60.06 (s), 35.74 (t), 35.33 (t), 34.68 (t), 32.77 (t), 28.43 (t), 25.14 (t), 23.31 (t). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.63; H, 10.28.

***endo*-Tricyclo[5.3.2.0^{1,7}]dodec-11-en-2-ol (17n).** A 5.70-g (23.1 mmol) sample of **15** was reduced with sodium and liquid ammonia as described above to give tricyclo[5.3.2.0^{1,7}]dodec-11-en-2-one (**16**): 1.35 g (33%); IR 3020, 1680, 750 cm^{-1}; MS, *m/e* (relative intensity) 176 (M$^+$, 61), 148 (50), 105 (49), 91 (100); ^{1}H NMR δ 0.96–2.40 (m, 13 H), 2.70 (dt, *J* = 3, 12 Hz, 1 H), 6.08 (s, 2 H). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.70; H, 9.26.

A 127-mg (0.72 mmol) sample of **16** was reduced by lithium aluminum hydride as described for **15** to give the endo alcohol **17n**: 116 mg (90%); mp 48–49 °C; IR (KBr) 3370, 3010, 1030, 740 cm^{-1}; MS, *m/e* (relative intensity) 178 (M$^+$, 55), 149 (100); ^{1}H NMR δ 1.10–1.92 (m, 15 H), 3.80 (m, 1 H), 5.90 (AB q, *J* = 3, 2 H); ^{13}C NMR δ 140.62 (d), 137.50 (d), 75.61 (d), 63.63 (s), 58.92 (s), 34.56 (t), 33.58 (t), 32.08 (t), 27.17 (t), 26.72 (t), 24.08 (t), 23.11 (t). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.70; H, 10.33.

***exo*-Tricyclo[5.3.2.0^{1,7}]dodecan-2-ol (8x).** A 641-mg (3.60 mmol) sample of the *exo*-propellenol **17x** was hydrogenated in 20 mL of methanol in the presence of a catalytic amount of 10% palladized charcoal at room temperature at 1 atm. After filtration, the filtrate was concentrated in vacuo, and the residue was chromatographed to give the exo alcohol **8x**: 571 mg (88%); mp 53–54 °C; IR (KBr) 3250, 1005 cm^{-1}; MS, *m/e* (relative intensity) 180 (M$^+$, 31), 152 (21), 151 (33), 137 (100); ^{1}H NMR δ 1.00–2.32 (m, 19 H), 3.40 (m, 1 H); ^{13}C NMR δ 78.61 (d), 54.37 (s), 48.83 (s), 43.50 (t), 41.30 (t), 38.01 (t), 35.52 (t), 27.65 (t), 25.28 (t), 24.33 (t), 24.04 (t), 19.97 (t). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.71; H, 10.94.

***endo*-Tricyclo[5.3.2.0^{1,7}]dodecan-2-ol (8n).** Hydrogenation of 53 mg (0.30 mmol) of the *endo*-propellenol **17n** as described for **17x** gave the endo alcohol **8n**: 46 mg (85%); mp 56–57 °C; IR (KBr) 3350, 1000 cm^{-1}; MS, *m/e* (relative intensity) 180 (M$^+$, 12), 152 (100), 151 (52), 137 (32); ^{1}H NMR δ 1.00–1.98 (m, 18 H), 2.06 (s, 1 H), 3.80 (m, 1 H); ^{13}C NMR δ 79.40 (d), 53.05 (s), 47.63 (s), 38.63 (t), 38.27 (t), 34.73 (t), 32.91 (t), 29.40 (t), 28.30 (t), 27.06 (t), 24.56 (t), 24.04 (t). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.55; H, 11.28.

***exo*- and *endo*-Tricyclo[4.3.2.0^{1,6}]undec-10-en-2-ol (21x and 21n).** A solution of 11.4 g (83.6 mmol) of the enone **18** in 280 mL of dichloroethylene was irradiated as described for **17x** to give the cycloadducts **19** (2:93:5 ratio): 18.3 g (94%); bp 126–135 °C (3 mm); IR 1700 cm^{-1}.

The above adducts (18.3 g) were reduced with sodium and liquid ammonia as described for **17x** to give tricyclo[4.3.2.0^{1,6}]undec-10-en-2-one (**20**):[18] 6.69 g (53%); IR 3010, 1690 cm^{-1}.

A 2.62-g (16.2 mmol) sample of **20** was reduced by lithium aluminum hydride as described for **15** to give a mixture of the crude alcohols **21x** and **21n** which was chromatographed (Merck silica gel 60, 70–230 mesh ASTM) to afford **21x** and **21n** (eluent; 30% and 15% ether–petroleum ether, respectively).

21x: 1.68 g (63%); mp 32–34 °C; IR (KBr), 3300, 3010, 1020, 740 cm^{-1}; MS, *m/e* (relative intensity) 164 (M$^+$, 19), 135 (50), 122 (100); ^{1}H NMR δ 0.82–1.96 (m, 13 H), 3.62 (dd, *J* = 5, 12 Hz, 1 H), 5.99 (s, 2 H); ^{13}C NMR δ 141.84 (d), 135.55 (d), 76.30 (d), 59.57 (s), 57.22 (s), 33.50 (t), 32.08 (t), 30.09 (t), 27.94 (t), 23.39 (t), 19.25 (t). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.47; H, 9.85.

21n: 0.61 g (23%); mp 36–37 °C; IR (KBr) 3300, 3010, 1020, 740 cm^{-1}; MS, *m/e* (relative intensity) 164 (M$^+$, 32), 146 (64), 118 (95), 117 (100); ^{1}H NMR δ 0.88–1.92 (m, 13 H), 3.93 (t, 1 H), 5.92 (s, 2 H); ^{13}C NMR δ 140.14 (d), 138.43 (d), 72.02 (d), 58.60 (s), 56.00 (s), 32.93 (t), 30.05 (t), 27.49 (t), 25.62 (t), 23.07 (t), 17.42 (t). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.38; H, 9.81.

***exo*- and *endo*-Tricyclo[4.3.2.0^{1,6}]undecan-2-ol (9x and 9n).** Respective hydrogenation of 734 mg (4.53 mmol) of **21x** and 577 mg (3.65 mmol) of **21n** as described for **17x** and **17n** gave the corresponding alcohols **9x** and **9n**.

(18) Cargill, R. L.; Crawford, J. W. *J. Org. Chem.* **1970**, *35*, 356.

9x: 628 mg (85%); mp 78–79 °C; IR (KBr) 3300, 1045 cm^{-1}; MS, *m/e* (relative intensity) 166 (M$^+$, 11), 138 (39), 123 (100), 110 (25); ^{1}H NMR δ 1.16–2.27 (m, 17 H), 3.38 (dd, *J* = 4, 12 Hz, 1 H); ^{13}C NMR δ 75.41 (d), 49.40 (s), 48.18 (s), 40.42 (t), 40.35 (t), 32.74 (t), 29.21 (t), 27.75 (t), 25.31 (t), 20.16 (t), 19.80 (t). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.06; H, 11.03.

9n: 491 mg (84%); mp 92–94 °C; IR (KBr) 3300, 1035 cm^{-1}; MS, *m/e* (relative intensity) 166 (M$^+$, 7), 138 (100), 110 (60); ^{1}H NMR δ 1.08–2.07 (m, 17 H), 3.83 (dd, *J* = 4, 10 Hz, 1 H); ^{13}C NMR δ 75.34 (d), 50.42 (s), 47.32 (s), 40.62 (t), 32.16 (t), 31.87 (t), 28.87 (t), 27.53 (t), 27.45 (t), 25.19 (t), 19.02 (t). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.10; H, 10.95.

Acid-Catalyzed Rearrangement of Propellanols 8x, 8n, 9x, and 9n. Acid-catalyzed reactions of the alcohols were carried out as described previously for [*m.n.*2]propellanones.[1b,5] (A) A solution of 500 mg of the alcohol, 0.5 mL of concentrated sulfuric acid, and 0.5 mL of water in 5 mL of tetrahydrofuran was stirred at 55 °C unless otherwise stated.[1b] (B) A solution of 300 mg of the alcohol and 0.6 mL of concentrated HCl in 6 mL of ether was stirred at reflux unless otherwise stated.[5] After usual workup, the crude products were purified by column chromatography.

(1*S,6*R**,7*S**)-Tricyclo[5.3.2.0^{1,6}]dodecan-7-ol (22).** The reaction of 233 mg (1.29 mmol) of **8x** by method A at room temperature for 24 h gave the alcohol **22**: 202 mg (87%); mp 73–75 °C; IR (KBr) 3350, 1050 cm^{-1}; MS, *m/e* (relative intensity) 180 (M$^+$, 23), 151 (31), 137 (100); ^{1}H NMR δ 0.80–2.00 (m); ^{13}C NMR δ 80.96 (s), 54.80 (d), 42.69 (s), 41.52 (t), 40.87 (t), 34.86 (t), 34.24 (t), 28.26 (t), 25.18 (t), 22.87 (t), 22.12 (t), 20.50 (t). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.69; H, 11.38.

(1*S,6*R**,7*S*)-7-Chlorotricyclo[5.3.2.0^{1,6}]dodecane (23).** The reaction of 312 mg (1.73 mmol) of **8x** by method B at room temperature for 24 h gave 246 mg (79%) of **22** and the chloride **23**: 41 mg (12%); IR 780 cm^{-1}; MS, *m/e* (relative intensity) 200 (M$^+$ + 2, 13), 198 (M$^+$, 39), 163 (100); ^{1}H NMR δ 0.80–2.36 (m); ^{13}C NMR δ 77.51 (s), 56.52 (d), 44.35 (t), 43.30 (s), 41.28 (t), 37.21 (t), 34.28 (t), 29.26 (t), 25.48 (t), 25.28 (t), 22.07 (t), 21.55 (t). Anal. Calcd for $C_{12}H_{19}Cl$: C, 72.52; H, 9.63. Found: C, 72.55; H, 9.49. To a 116-mg (0.64 mmol) sample of **22** cooled in an ice bath was added 1.7 mL of thionyl chloride via a syringe. The solution was stirred at room temperature for 4 h. Ice–water was added carefully, and the mixture was extracted with ether. The extracts were washed with saturated $NaHCO_3$ solution, brine, and dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was chromatographed to give 105 mg (82%) of a chloride. The ^{13}C NMR spectrum of the chloride was identical with that of **23**.

(1*S,6*S**,7*S**)-Tricyclo[5.3.2.0^{1,6}]dodecan-7-ol (24).** The reaction of 200 mg (1.11 mmol) of **8n** by method A for 48 h gave the alcohol **24**: 153 mg (77%); mp 62–63 °C; IR (KBr) 3350, 1080 cm^{-1}; MS, *m/e* (relative intensity) 180 (M$^+$, 28), 157 (100), 137 (67); ^{1}H NMR δ 0.77 (m, 1 H), 0.92–2.00 (m, 19 H); ^{13}C NMR δ 79.36 (s), 53.50 (d), 41.36 (s), 39.05 (t), 36.81 (t), 35.54 (t), 32.55 (t), 27.94 (t), 26.02 (t), 21.93 (t), 20.21 (t), 19.82 (t). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.57; H, 11.29.

(1*S,6*S**,7*S**)-7-Chlorotricyclo[5.3.2.0^{1,6}]dodecane (25).** The reaction of 328 mg (1.82 mmol) of **8n** by method B for 24 h gave 255 mg (78%) of **24** and the chloride **25**: 36 mg (10%); IR 780 cm^{-1}; MS, *m/e* (relative intensity) 200 (M$^+$ + 2, 8), 198 (M$^+$, 22), 163 (100), 135 (35), 121 (22); ^{1}H NMR δ 0.78 (m, 1 H), 0.82–2.20 (m, 18 H); ^{13}C NMR δ 75.03 (s), 55.64 (d), 41.49 (s), 39.02 (t), 38.98 (t), 36.17 (t), 35.33 (t), 27.35 (t), 25.89 (t), 21.75 (t), 21.25 (t), 19.90 (t). Anal. Calcd for $C_{12}H_{19}Cl$: C, 72.52; H, 9.63. Found: C, 72.47; H, 9.85. Chlorination of 411 mg (2.28 mmol) of **24** as described for **22** gave 410 mg (90%) of a chloride which was identical (^{13}C NMR) with **25**.

(1*S,5*R**,6*S**)-Tricyclo[4.3.2.0^{1,5}]undecan-6-ol (32).** The reaction of 123 mg (0.74 mmol) of **9x** by method A for 24 h gave the alcohol **32**: 102 mg (83%); mp 74–75 °C; IR (KBr) 3325, 1050 cm^{-1}; MS, *m/e* (relative intensity) 166 (M$^+$, 24), 123 (100); ^{1}H NMR δ 0.96–2.02 (m); ^{13}C NMR δ 81.87 (s), 60.51 (d), 52.89 (s), 40.96 (t), 37.30 (t), 36.84 (t), 34.87 (t), 31.60 (t), 25.19 (t), 22.70 (t), 21.53 (t). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.37; H, 10.73.

(1*S,5*R**,6*S**)-6-Chlorotricyclo[4.3.2.0^{1,5}]undecane (33).** The reaction of 333 mg (2.01 mmol) of **9x** by method B for 24 h gave 213 mg (64%) of **32** and the chloride **33**: 69 mg (19%); IR 790 cm^{-1}; MS, *m/e* (relative intensity) 186 (M$^+$ + 2, 6), 184

(M^+, 17), 156 (65), 149 (84), 121 (100); ^1H NMR δ 1.06–2.46 (m); ^{13}C NMR δ 75.90 (s), 62.90 (d), 52.93 (s), 43.98 (t), 37.45 (t), 37.16 (t, 2C), 32.70 (t), 27.40 (t), 22.26 (t), 21.85 (t). Anal. Calcd for $C_{11}H_{17}Cl$: C, 71.53; H, 9.28. Found: C, 71.50; H, 9.26. Chlorination of 69 mg (0.42 mmol) of **32** as described for **22** gave 57 mg (74%) of a chloride which was identical (^{13}C NMR) with **33**.

(1*S,5*R**,6*S*)-Tricyclo[4.3.2.0^{1,5}]undecan-5-ol (38) and *cis*,*cis*-Tricyclo[6.3.0.0^{1,5}]undecan-5-ol (39).** The reaction of 176 mg of **9n** by method A for 24 h gave the two alcohols **38** and **39**.

38: 48 mg (27%); mp 67–69 °C; IR (KBr) 3400, 900 cm^{-1}; MS, *m/e* (relative intensity) 166 (M^+, 43), 109 (57), 97 (100), 96 (54), 95 (55), 84 (58); ^1H NMR δ 0.95–2.30 (m); ^{13}C NMR δ 87.06 (s), 50.32 (s), 41.30 (d), 35.94 (t), 33.65 (t), 32.16 (t), 31.35 (t), 26.77 (t), 24.77 (t), 20.46 (t), 17.75 (t). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.14; H, 11.08.

39: 93 mg (53%); mp 33–35 °C; IR (KBr) 3350, 1040 cm^{-1}; MS, *m/e* (relative intensity) 166 (M^+, 8), 124 (100); ^1H NMR δ 0.90–2.24 (m); ^{13}C NMR δ 89.97 (s), 62.05 (s), 52.18 (d), 41.84 (t), 41.16 (t), 40.47 (t), 35.47 (t), 34.30 (t), 30.01 (t), 27.45 (t), 23.63 (t). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.06; H, 10.98.

The reaction of 212 mg (1.28 mmol) of **9n** by method A for 72 h gave 14 mg (7%) of **38** and 133 mg (63%) of **39**. Also, the reaction of 50 mg (0.30 mmol) of **38** by method A for 72 h gave **39** in quantitative yield.

***cis*,*cis*-5-Chlorotricyclo[6.3.0.0^{1,5}]undecane (40).** The reaction of 304 mg (1.83 mmol) of **9n** by method B for 24 h gave 72 mg (23%) of **38**, 23 mg (8%) of **39**, and the chloride **40**: 137 mg (41%); IR 755 cm^{-1}; MS, *m/e* (relative intensity) 186 (M^+ + 2, 31), 184 (M^+, 85), 149 (70), 148 (73), 120 (90), 119 (100), 107 (85), 79 (71); ^1H NMR δ 1.16–2.40 (m); ^{13}C NMR δ 86.33 (s), 64.56 (s), 52.15 (d), 43.89 (t), 42.69 (t), 40.81 (t), 39.18 (t), 34.43 (t), 30.38 (t), 27.06 (t), 23.77 (t). Analytical data were not obtained because of the lability of **40** under preparative GLC conditions. Chlorination of 2.13 g (12.8 mmol) of **39** gave 1.97 g (83%) of a chloride which was identical (MS, ^{13}C NMR) with **40**.

(1*S,6*R**,7*S**)-Tricyclo[5.3.2.0^{1,6}]dodecane (26).** To a stirred solution of 400 mg (2.02 mmol) of the chloride **23** and 400 mg of azobis(isobutyronitrile) in 7 mL of cyclohexane was added dropwise a solution of 1.18 g (4.04 mmol) of tri-*n*-butyltin hydride in 14 mL of cyclohexane at room temperature under nitrogen. The solution was heated at reflux for 3 h and concentrated in vacuo. The residue was distilled under reduced pressure (70–100 °C (40 mm)) to give the hydrocarbon **26** which was purified by column chromatography: 180 mg (54%); IR 2910, 2850 cm^{-1}; MS, *m/e* (relative intensity) 164 (M^+, 41), 136 (75), 121 (100), 79 (51); ^1H NMR δ 0.82–2.16 (m); ^{13}C NMR δ 52.22 (d), 42.60 (s + t), 41.46 (d), 34.19 (t), 33.71 (t), 29.56 (t), 27.78 (t), 27.61 (t), 25.99 (t), 22.29 (t), 19.98 (t). Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.70; H, 12.30.

(1*S,6*S**,7*S**)-Tricyclo[5.3.2.0^{1,6}]dodecane (27).** A 413-mg (2.08 mmol) sample of the chloride **25** was reduced with tri-*n*-butyltin hydride as described for **23** to give the hydrocarbon **27**: 274 mg (80%); IR 2900, 2850 cm^{-1}; MS, *m/e* (relative intensity) 164 (M^+, 45), 136 (85), 135 (100), 121 (76); ^1H NMR δ 0.80–2.16 (m); ^{13}C NMR δ 48.86 (d), 40.23 (s), 39.57 (t), 38.59 (d), 37.89 (t), 29.45 (t), 28.50 (t), 26.99 (t), 25.62 (t), 23.16 (t), 22.53 (t), 19.41 (t). Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.80; H, 12.38.

Preparations of Authentic Samples of 26 and 27. (1*S,6*R**,7*S**)-7-Chlorotricyclo[5.3.2.0^{1,6}]dodecan-6-ol (3c).** The reaction of 16.5 g (92.7 mmol) of [5.3.2]propellanone (**1**) by method B for 2 h gave the alcohol **3c**: 17.0 g (86%); mp 34 °C; IR (KBr) 3450, 1010, 780 cm^{-1}; MS, *m/e* (relative intensity) 216 (M^+ + 2, 7), 214 (M^+, 20), 178 (89), 111 (79), 98 (100); ^1H NMR δ 0.78–2.56 (m); ^{13}C NMR δ 80.02 (s), 78.41 (s), 42.81 (s), 37.62 (t), 34.28 (t), 33.79 (t), 32.06 (t), 31.21 (t), 27.04 (t), 21.41 (t), 21.21 (t), 20.41 (t). Anal. Calcd for $C_{12}H_{19}ClO$: C, 74.19; H, 9.54. Found: C, 74.09; H, 9.35.

7-Chlorotricyclo[5.3.2.0^{1,6}]dodec-5-ene (28). To a stirred solution of 6.72 g (31.3 mmol) of **3c** in 15 mL of pyridine and 60 mL of methylene chloride was added 3.41 mL (47.0 mmol) of thionyl chloride via a syringe at 0 °C, and then the mixture was stirred at 0 °C for an additional 30 min. After being stirred at room temperature for 4 h, ice–water was added carefully. The organic layer was separated and the aqueous solution was extracted with methylene chloride. The combined organic layer was washed with 5% HCl, saturated $NaHCO_3$ solution, and water, successively, and then dried ($MgSO_4$). The solvent was removed in vacuo and the residue was chromatographed to give the chloride **28**: 5.95 g (97%); IR 3020, 800, 690 cm^{-1}; MS, *m/e* (relative intensity) 198 (M^+ + 2, 3), 196 (M^+, 10), 161 (100), 91 (13); ^1H NMR δ 1.00–2.32 (m, 16 H), 5.60 (t, 1 H); ^{13}C NMR δ 148.75 (s), 112.97 (d), 73.18 (s), 44.79 (t), 41.34 (s), 38.50 (t), 38.33 (t), 35.53 (t), 35.33 (t), 44.29 (t), 21.40 (t), 19.86 (t). Anal. Calcd for $C_{12}H_{17}Cl$: C, 73.27; H, 8.71. Found: C, 73.27; H, 8.83.

Tricyclo[5.3.2.0^{1,6}]dodec-5-ene (29). A 5.06-g (25.8 mmol) sample of **28** was reduced by tri-*n*-butyltin hydride as described for **23** to give the olefin **29**: 3.99 g (96%); IR 800 cm^{-1}; MS, *m/e* (relative intensity) 162 (M^+, 100), 134 (61), 133 (53), 119 (59), 91 (66); ^1H NMR δ 1.03–2.02 (m, 16 H), 2.30–2.5 6 (m, 1 H), 5.20 (t, 1 H); ^{13}C NMR δ 150.51 (s), 110.74 (d), 41.83 (d), 40.77 (s), 40.16 (t), 36.43 (t), 35.33 (t), 35.09 (t), 27.74 (t), 25.01 (t), 20.43 (t), 19.78 (t). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.63; H, 11.44.

(1) Hydrogenation of 430 mg (2.65 mmol) of **29** as described above gave 380 mg (87%) of two hydrocarbons in a 1:1 ratio which were identical (^{13}C NMR) with **26** and **27**, respectively.

(2) To a suspension of 4.50 g (27.7 mmol) of **29** and 0.52 g (13.7 mmol) of sodium borohydride in 20 mL of dry tetrahydrofuran was added 2.23 mL (15.7 mmol) of boron trifluoride etherate under nitrogen. The mixture was stirred at room temperature for 5 h, and then 1.6 mL of water, 4.6 mL of 3 N sodium hydroxide solution, and 4.6 mL of 30% hydrogen peroxide were added successively. The reaction mixture was left overnight and extracted with ether. The extracts were washed with brine and dried ($MgSO_4$). The solvent was removed in vacuo to give the crude alcohols; IR 3300 cm^{-1}.

To a stirred solution of 25.1 g (0.32 mol) of pyridine in 350 mL of methylene chloride was added 16.6 g (0.16 mol) of chromium trioxide with cooling by an ice bath. The deep burgundy solution was stirred for 15 min at room temperature. Then, a solution of the above alcohols in 50 mL of methylene chloride was added. After being stirred for an additional 1 h at room temperature, the solution was decanted and the residue was washed with methylene chloride. The combined organic solutions were washed with two portions of 10% sodium hydroxide solution, 5% HCl, saturated $NaHCO_3$ solution, and brine, successively. After drying ($MgSO_4$), the solvent was removed in vacuo to give the two ketones **30** and **31** in ~1:4 ratio by GLC. Chromatography on activated alumina (Wako Pure Chemical Industries, Alumina, activated, 200 mesh) afforded only **30**.

30: 3.82 g (77% from 29); IR 1710 cm^{-1}; MS, *m/e* (relative intensity) 178 (M^+, 82), 123 (73), 110 (100), 79 (42); ^1H NMR δ 1.00–2.30 (m, 17 H), 2.56 (m, 1 H); ^{13}C NMR δ 211.58 (s), 63.62 (d), 49.10 (s), 41.68 (t), 41.25 (t), 34.31 (d), 32.81 (t), 32.05 (t), 29.85 (t), 26.94 (t), 23.29 (t), 19.15 (t). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.48; H, 10.26.

31. An analytical sample of **31** was obtained from the crude product mixture by preparative GLC; IR 1710 cm^{-1}; MS, *m/e* (relative intensity) 178 (M^+, 72), 123 (49), 110 (100); ^1H NMR δ 0.80–2.52 (m); ^{13}C NMR δ 214.47 (s), 59.48 (d), 46.36 (s), 40.82 (t), 37.27 (t), 36.36 (t), 34.21 (d), 31.57 (t), 27.59 (t), 25.01 (t), 23.29 (t), 18.98 (t). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.72; H, 10.24.

A solution of 348 mg (1.96 mmol) of **30** and a small amount of hydroquinone in 1.5 mL of ethane-1,2-dithiol was added dropwise to 1 mL of boron trifluoride etherate cooled in an ice bath. The resulting solution was stirred at room temperature for 48 h. The reaction was quenched by 10% K_2CO_3 solution, and the mixture was extracted with benzene. The extracts were washed with brine, dried (K_2CO_3), and concentrated in vacuo to give the crude ethylene dithioketal: IR 1280, 1200 cm^{-1}.

A solution of the above thioketal in 50 mL of ethanol was heated at reflux for 3 h with about 5 g of Raney nickel (W-4). The mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The residue was chromatographed to give 182 mg (57%) of a hydrocarbon which was identical (MS, ^{13}C NMR) with **26**.

(1*S,5*R**,6*S**)-Tricyclo[4.3.2.0^{1,5}]undecane (34).** A 530-mg (2.82 mmol) sample of chloride **33** was reduced with tri-*n*-butyltin hydride as described for **23** to give the hydrocarbon **34**: 300 mg

(70%); waxy solid; IR (KBr) 2920, 2850 cm^{-1}; MS, *m/e* (relative intensity) 150 (M^+, 17), 122 (100), 121 (37), 93 (22), 80 (26); ^1H NMR δ 1.03–2.24 (m); ^{13}C NMR δ 57.32 (d), 51.69 (s), 39.87 (d), 38.84 (t), 36.16 (t), 33.72 (t), 33.47 (t), 27.14 (t, 2C), 22.72 (t), 19.75 (t). Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.80; H, 12.18.

Preparation of an Authentic Sample of 34. Hydroboration–oxidation of 478 mg (3.23 mmol) of the tricyclic olefin **35**[5] and subsequent Collins oxidation of the resulting alcohols as described above gave two crude ketones **36** and **37** in an about 1:1 ratio (IR 1735 cm^{-1}). Upon chromatography on activated alumina, only ketone **36** was isolated: 380 mg (72% from **35**); mp 32 °C; IR (KBr) 1735 cm^{-1}; MS, *m/e* (relative intensity) 164 (M^+, 100), 122 (72), 120 (64), 107 (65), 80 (71), 79 (71); ^1H NMR δ 1.10–2.20 (m, 15 H), 2.48–2.68 (m, 1 H). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.27; H, 9.90. The other ketone, presumably **37**, was not characterized owing to its lability (isomerization to **36**) during separation.

A solution of 286 mg (1.74 mmol) of **36**, 0.5 g of potassium hydroxide, and 0.5 mL of hydrazine hydrate in 5 mL of diethylene glycol was heated at 150 °C for 3 h. The excess hydrazine was distilled off, and the resulting solution was heated at ca. 200 °C for an additional 4 h; 5% HCl was added to the cooled solution, and the mixture was extacted with ether. The extracts were dried ($MgSO_4$) and concentrated in vacuo carefully. The residue was chromatographed to give 98 mg (37%) of a hydrocarbon which was identical (MS, ^{13}C NMR) with **34**.

***cis,cis*-Tricyclo[6.3.0.0^{1,5}]undecane (41).**[15] A 688-mg (3.73 mmol) of the chloride **40** was reduced with tri-*n*-butyltin hydride as described for **23** to give the hydrocarbon **41**: 517 mg (92%); MS, *m/e* (relative intensity) 150 (M^+, 16), 122 (100), 121 (34), 107 (75), 79 (42); ^{13}C NMR δ 61.95 (s), 52.36 (d, 2C), 42.13 (t, 2C), 33.52 (t, 4C), 26.84 (t, 2C), (lit.[15] δ 62.0, 52.4, 42.1, 33.6, 33.5, 26.8).

Preparation of an Authentic Sample of 38. A 1.32-g (6.57 mmol) sample of the tricyclic alcohol **4c**[5] was reduced with tri-*n*-butyltin hydride as described for **23** to give 1.10 g (100%) of a alcohol which was identical (mp, IR, ^{13}C NMR) with **38**.

Registry No. 1, 42540-18-1; **3c**, 94250-28-9; **4c**, 94345-88-7; **8x**, 94250-29-0; **8n**, 94345-89-8; **9x**, 92470-83-2; **9n**, 92406-68-3; **14**, 13031-01-1; **15** cis–anti–trans, 94278-63-4; **15** cis–syn–trans, 94346-34-6; **16**, 94250-30-3; **17x**, 94250-31-4; **17n**, 94345-90-1; **18**, 22118-01-0; **19**, 94250-32-5; **20**, 22241-68-5; **21x**, 94346-35-7; **21n**, 94250-44-9; **22**, 94346-36-8; **23**, 94250-33-6; **24**, 94250-34-7; **25**, 94345-91-2; **26**, 62859-77-2; **27**, 62797-91-5; **28**, 94250-35-8; **29**, 94250-36-9; **30**, 94250-37-0; **30** ethylene dithioketal deriv, 94250-38-1; **31**, 94345-92-3; **32**, 94250-39-2; **33**, 94250-40-5; **34**, 64822-62-4; **35**, 94250-41-6; **36**, 94250-42-7; **38**, 92406-69-4; **39**, 92406-70-7; **40**, 94250-43-8; **41**, 61950-20-7; *trans*-1,2-dichloroethylene, 156-60-5; *cis*-1,2-dichloroethylene, 156-59-2.

Static and Dynamic Stereochemistry of Tetra(primary alkyl)ethylenes

Leif Andersen,[†] Ulf Berg,*[‡] and Ingrid Pettersson[‡]

Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden, and Organic Chemistry 3, Chemical Center, University of Lund, S-221 00 Lund, Sweden

Received July 13, 1984

The stereochemistry of tetraethyl- (**1**), tetrapropyl- (**2**), tetraisobutyl- (**3**), tetraneopentyl- (**4**), and tetrabenzylethylene (**5**) has been investigated by dynamic ^1H NMR spectroscopy, X-ray analysis (for **5**), and molecular mechanics calculations (MM2, MMP2 force fields). The benzyl groups of **5** project alternately above and below the least-squares ethylene plane in the crystal. The NMR spectra of **3** and **4** are in agreement with a similar up-and-down conformation and molecular mechanics calculations predict ground-state structures of the same type (D_2 symmetry) for **1**–**4** but not for **5**. Arguments are presented that the molecular mechanics force field fails to reproduce the interaction potential for two benzene rings, leading to unreliable calculated conformational stabilities of **5**. The barrier ($\Delta G^{\ddagger}_{T_c}$) to site exchange of the alkyl groups in **1**, **2**, and **5** is ≤6.5 kcal/mol, in **3** is 8.6 kcal/mol, and in **4** is 19.8 kcal/mol ($\kappa = {}^1/_2$), in the latter case rectifying an earlier reported value. A gas-phase NMR study of **4** indicates that the barrier is at least 1.5 kcal/mol higher than that in solution. According to the calculations the alkyl group rotations are not concerted and the calculated barrier of **3** is in excellent agreement with the experimental value. Relative rates of epoxidation by *m*-chloroperbenzoic acid, obtained by a competition method, are as follows: 1-octene 0.4 ± 0.5, **1** 17 ± 5, **2** 16 ± 2, **3** 1.0, and **5** 0.003 ± 0.001; **4** was inert under the reaction conditions.

Sterically congested molecules have attracted considerable interest both as synthetic targets and as subjects for investigations of structure and physicochemical properties.[1] One such class of compounds is tetraalkylethylenes, with tetraisopropylethylene[2] and the hitherto elusive tetra-*tert*-butylethylene as notable representatives. These molecules have attracted interest for somewhat different reasons. Tetra-*tert*-butylethylene is predicted to be highly strained, with a calculated (molecular mechanics, MMI) strain energy of 100 kcal/mol, and to be twisted by ca. 45° around the double bond.[3,4] Tetraisopropylethylene, on the other hand, is not exceptionally strained (strain energy 18 kcal/mol), is planar, and has a "gear-meshed" conformation (C_{2h} symmetry).[4-6]

This report deals with the stereochemical features of some tetra(primary alkyl)ethylenes, of which two, tetrabenzyl-[7] and tetraneopentylethylene[8] have been investigated previously. The study covers dynamic ^1H NMR spectroscopy, X-ray crystallography, molecular mechanics

[†] Chalmers University of Technology.
[‡] University of Lund.

(1) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.
(2) (a) Langler, R. F.; Tidwell, T. T. *Tetrahedron Lett.* **1975**, 777. (b) Bomse, D. S.; Morton, T. H. *Ibid.* **1975**, 781.
(3) Lenoir, D.; Dauner, H.; Frank, R. M. *Chem. Ber.* **1980**, *113*, 2636.
(4) Favini, G.; Simonetta, M.; Todeschini, R. *J. Comput. Chem.* **1981**, *2*, 149.
(5) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.
(6) Ermer, O. *Angew. Chem.* **1983**, *95*, 1010; *Angew. Chem. Suppl.* **1983**, 1353.
(7) Richardson, W. H.; Gunderson, K. W. *J. Org. Chem.* **1976**, *41*, 2054.
(8) Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1977**, *42*, 580.

0022-3263/85/1950-0493$01.50/0